CHARACTERISTICS OF DIOXIN FORMATION IN MIXED INCINERATION OF MUNICIPAL SOLID WASTE WITH COAL

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Introduction

It has been reported that cofiring coal with municipal solid waste has the potential to suppress the formation of polychlorinated dibenzo-*p*-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs).[1] The primary suppression mechanism is believed to be the effect of sulfur (S) in the coal, converting the major chlorinator Cl_2 into HCl, which does not as readily form chlorinated hydrocarbons.[1, 2] In this study, the characteristics of PCDD/DF formation in the incineration of artificial solid wastes (ASW) with high-sulfur coal (HSC) or low-sulfur coal (LSC) was examined using a laboratory-scale fluidized-bed incinerator. The results suggest that S in ASW indeed inhibits PCDD/DF generation, although the presence of substances such as Fe and Na in ASW counteract the effect. The correlation between PCDD/DF, CO and total hydrocarbons (THC) emission in the combustion of ASW with higher coal contents is also investigated.

Experimental Method

Figure 1 is a schematic of the laboratory-scale experimental incinerator used in the experiments. This incinerator was designed so as to allow factors such as the air ratio and temperature to be varied independently. The primary combustor was made of quartz with an internal diameter of 74 mm and a height of 1100 mm. The secondary combustor was a high-alumina tube with an internal diameter of 100 mm and a height of 2000 mm. The temperature of the combustors was controlled using an electric heater, maintained at 800 °C and 900 °C, respectively. The flow rates of primary and secondary air were set to be identical and the total excess air ratio was kept at $\lambda = 2.0$. The feed rate of ASW was about 11 g/min. Flue gas was cooled by passage through a gas cooling section. The cooling section had an internal diameter of 83 mm and a length of 3000 mm, and was maintained at 300 °C using a water cooler and electric heater. The concentrations of O_2, CO and NOx in the flue gas were continuously monitored at location S5. PCDD/DF and gas sampling was conducted over 2

hours at location S3. O_2, CO, and NOx concentrations were measured using a zirconia, non-dispersive infrared (NDIR), and chemiluminescence gas analyzer, respectively (Horiba PG-250). The methane equivalent total hydrocarbons (THC) was using a flame ionization detector (FID) (Horiba MEXA-1110FRF).

The main components used for the base ASW were paper powder (45%), wood powder (20%), flour (15%), and PE powder (20%). In order to restrict the Cl content to as low as possible, unbleached paper, pine wood, salt-free flour and virgin resin PE were chosen as the components. To adjust the Cl contents, PVC or NaCl were added to the base ASW, and the ratio of S and fixed carbon was adjusted by adding HSC or LSC. The properties and elementary composition of the base ASW and ASW1 ~ ASW6 are given in Table 1.

Results and Discussion

The relationship between SO_X and PCDD/DF emissions for the incineration of base ASW and ASW1 ~ ASW6 is shown in Fig. 2. The effect of the addition of PVC and NaCl, indicated by the solid symbols in the figure, is insignificant as a result of the relatively higher air ratio of combustion. The effects of the air ratio on PCDD/DF generation are reported elsewhere as part of this symposium.[3] The combined effects of the addition of coal and a Cl source, on the other hand, are complicated. The combustion of ASW4 and ASW5 produces 300 ~ 350 ng/m^3 PCDD/DF. These ASWs contain HSC and a fair amount of Fe, as shown in Table 1. Fe has a catalytic effect for dioxin formation[4, 5] and is likely to promote the production of Cl_2 through a reaction similar to the Deacon process.[2] According to X-ray diffraction (XRD) analysis, Fe exists as $CaFe_5AlO_9$ in the HSC. As LSC contains less Fe, the combustion of ASW6, which includes LSC, results in almost the same level of PCDD/DF generation as for base ASW. Therefore, the difference in PCDD/DF concentration for the same level of SOx concentration (Fig. 2) is attributable to the effect of Fe. Although ASW3 contains much higher amounts of HSC than ASW5, PCDD/DF emission in the incineration of ASW3 is lower than for ASW5. This appears to be directly attributable to the suppressing effect of S; S converts Cl_2 into HCl, which is less likely to form chlorinated hydrocarbons, by the following reaction:

$$SO_2 + Cl_2 + H_2O \rightarrow SO_3 + 2HCl$$
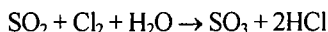
This reaction takes place in the gas phase and the suppressant is SO_2 and not solid compounds of sulfur. Therefore, the variation in PCDD/DF concentration with SOx concentration in Fig. 2 is due to SO_2. ASW4, having the same HSC content as ASW3, exhibits the same PCDD/DF levels as ASW5 because the Na in ASW4 forms stable compounds with S and prevents the generation of SO_2, as shown in Fig. 3. Therefore, sulfur has the potential to suppress PCDD/DF generation, however the effect is limited by the presence of substances such as Fe and Na.

Figures 4 and 5 show the relationships between PCDD/DF and CO, and PCDD/DF and THC, for the incineration of ASW1 and ASW6 with 4% PVC under various excess air ratios. In the case of ASW1 (solid symbols), good correlations for PCDD/DF-CO and PCDD/DF-THC are observed. For ASW6, however, the CO concentration remains elevated despite maintaining the good correlation for PCDD/DF-THC. Figure 6 shows the histories of the O_2, CO and THC concentrations for the incineration of ASW1 at $\lambda = 1.7$ and ASW6 at $\lambda = 2.0$. These two test produced the same average CO concentrations. From the figure, the

combustion of ASW6 at $\lambda = 2.0$ yields neither peak of CO nor THC, and the formation of PCDD/DF is consequently inhibited, as shown in Fig. 2. The effects of heterogeneities, which are thought to be responsible for peaks, on PCDD/DF formation are reported elsewhere as part of this symposium.[3]

Acknowledgements

References

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4) L. Stieglitz, H. Vogg, ISWA88. Proceeding of the 5th Int. Solid Wastes Conference, Vol.1, 331-335 (1988).

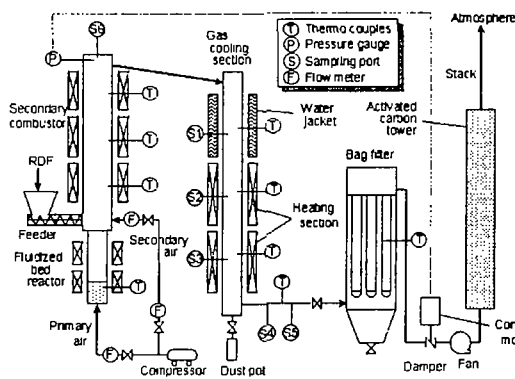5) H. Ismo, T. Kari, R. Juhani, Chemosphere, Vol.34, 2649-2662 (1997).

Fig. 1 Schematic of laboratory-scale experimental incinerator.

Table 1 Properties and elementary compositions of ASW

ASW No.		Base	1	2	3	4	5	6
PVC	wt% DB	0	4	0	4	0	4	4
NaCl	wt% DB	0	0	4	0	4	0	0
HSC	wt% DB	0	0	0	20	20	6.5	0
LSC	wt% DB	0	0	0	0	0	0	60
Moisture	wt% WB	6.1	5.7	6.0	5.5	5.7	7.2	4.6
Ash content	wt% DB	5.3	5.0	5.9	9.8	11.8	7.2	7.0
Volatile matter	wt% DB	83.7	80.9	80.6	61.6	64.1	75.4	46.9
Fixed carbon	wt% DB	11.0	14.1	13.5	28.6	24.1	17.4	46.1
C	wt% DB	51.5	51.9	51.7	53.9	53.7	51.1	65.7
H	wt% DB	7.7	7.6	7.5	6.9	6.9	7.0	5.3
N	wt% DB	0.31	0.30	0.28	0.51	0.54	0.40	1.23
S	wt% DB	0.02	0.02	0.02	0.43	0.50	0.14	0.13
Cl	wt% DB	0.04	1.64	1.90	2.04	1.84	2.26	2.23
O	wt% DB	35.1	33.5	32.7	26.4	24.7	32.0	18.5
Na	wt% DB	0.02	0.02	1.29	0.12	1.15	0.08	0.04
Cu	mg/kg DB	<1	<1	<1	20	10	10	30
Fe	mg/kg DB	360	330	340	3990	3390	1200	610
HHV	kcal/kg	5500	5560	5370	5280	5440	5410	6320
LHV	kcal/kg	5090	5150	4960	4910	5070	5040	6040

● Base ASW ◆ ASW1 (PVC4%) ■ ASW2 (NaCl4%) ◇ ASW3 (PVC4%+HSC20%)
□ ASW4 (NaCl4%+ASW20%) △ ASW5 (PVC4%+HSC6.5%) ○ ASW6 (PVC4%+LSC60%)
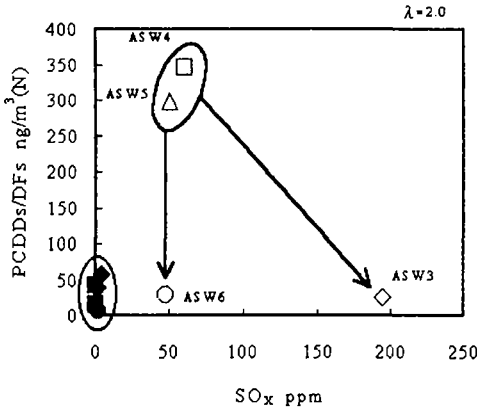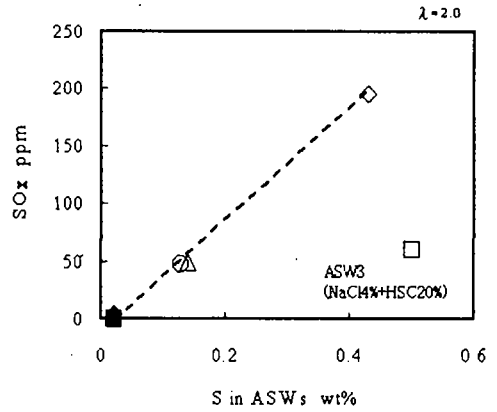

Fig. 2 Relationship between SO_X and PCDD/DF

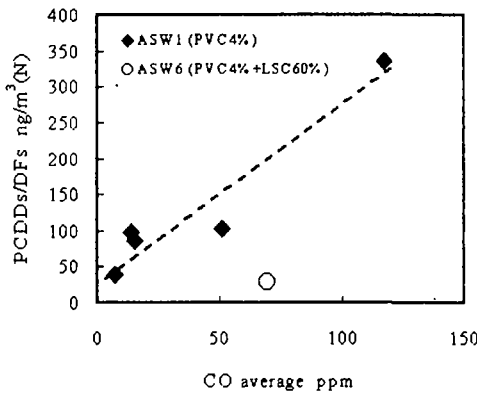Fig. 3 Relationship between sulfur in ASW and SO_X

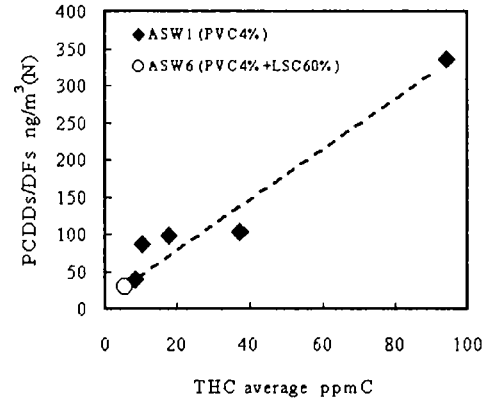Fig. 4 Correlation between CO and PCDD/DF
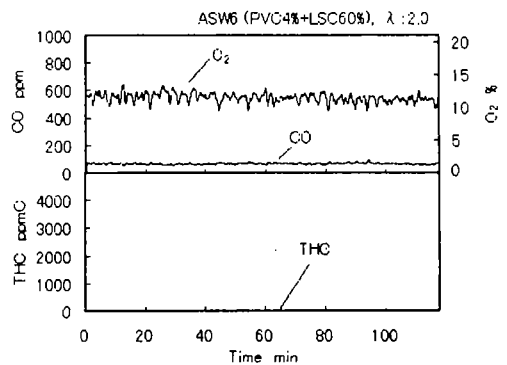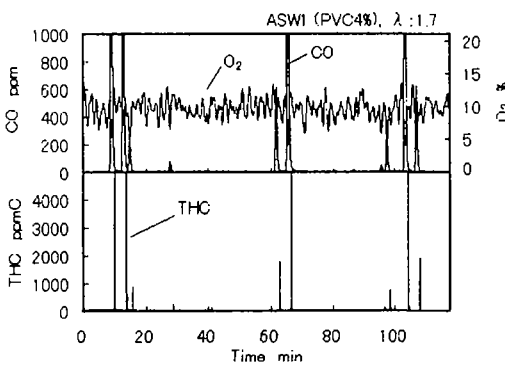

Fig. 5 Correlation between THC and PCDD/DF

Fig. 6 Levels of O_2, CO and THC